Hydrate Phase Equilibria of the Carbon Dioxide, Methane and Water System

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Abstract

Three-phase equilibria for the carbon dioxide – methane – water system were obtained by employing the isobaric temperature search method. Based on these isobaric hydrate equilibrium studies, the ternary hydrate, water-rich liquid and vapor equilibrium lines generated at different compositions of carbon dioxide and methane were all placed between two binary lines of simple hydrates formed by single guest component. The upper quadruple points where the four phases, hydrate, water-rich liquid, CO_2-rich liquid and vapor phases, coexist were measured at the composition range of 100 to 82.50 carbon dioxide mole %. Below 82.50 mole % of carbon dioxide the upper quadruple points were not possible to exist because methane can't be liquefied at the hydrate equilibrium range considered in this study. In addition, two-phase equilibria of vapor and hydrate were also determined at three different pressures of 20, 26 and 35 bar. Judging from the resulting T-x diagram, the concentration of carbon dioxide in hydrate phase was found to be higher than 90 mole % when the corresponding equilibrium vapor phase composition maintained to be higher than 40 mole % carbon dioxide. The carbon dioxide concentration and relative selectivity over methane in the hydrate phase appeared to increase with decreasing pressure.

Introduction

Gas hydrates are crystalline compounds that are formed by physically stable interaction between water and relatively small guest molecules occupied in the cavities built by water molecules. Recently, gas hydrates have attracted the attention of many investigators of petroleum, chemical engineering and environmental science from a different point of view. One of attractive application of gas hydrates is the sequestration of carbon dioxide in the form of solid hydrates. The suggested strategy is the ocean sequestration of carbon dioxide by direct injection to create a long-lived carbon dioxide hydrate lake on the ocean floor. Vast amount of natural gas composed of largely methane and other hydrocarbons has been known to exist in the marine sediments of ocean floor and permafrost zone as a hydrate state[1]. Carbon dioxide hydrates may also form naturally in this region if an appropriate condition of temperature and pressure is provided. Carbon dioxide injection to natural gas hydrate deposits results in the dissociation of methane hydrates. Therefore, it might be reasonable to suggest that the carbon dioxide sequestration into marine sediments can be simultaneously performed together with natural gas exploitation. To achieve the replacement of methane by carbon dioxide in the hydrate state it becomes essential to determine the hydrate phase equilibria containing two guest components of carbon dioxide and methane. Until now only a few studies have been carried out for treating this mixture system. Unruh and Katz reported the phase equilibrium data of this mixture and determined the vapor phase concentrations indirectly[2]. Berecz and Balla-Achs found that the mixed hydrates of carbon dioxide and methane exhibited instability in the region of carbon dioxide mole fraction of 50% and higher[3]. Adisasmito et al. extended the data of Unruh and Katz and showed that the result of Berecz and Balla-Achs was very unusual[4]. Dholabhai et al in

1994 measured the three phase (hydrate, water-rich liquid and vapor) equilibrium conditions in both pure water and electrolyte solutions containing NaCl, KCl and $CaCl_2$. These electrolytes caused the inhibition effect on hydrate formation[5]. In 1995 Ohgaki et. al. measured three phase equilibria at isothermal conditions and reported the thermodynamic relationship among pressure, gas phase composition and hydrate composition. They also briefly discussed the possibility of natural gas exploitation and carbon dioxide isolation[6]. In 1999 Servio et. al measured the incipient equilibrium hydrate formation conditions at two different compositions of 80-20% and 50-50% methane-carbon dioxide mixtures in the presence of neohexane. It was found that the 80-20 gas mixture forms structure H hydrate. The results from the 50-50 mixture indicate that above approximately 277.5 K structure I hydrate are formed. Below that temperature, a transition state occurs resulting in structure H or a mixture of structure H and I hydrates[7].

In particular, the isobaric three-phase, hydrate, water-rich liquid and vapor ($H-L_w-V$) equilibrium conditions of carbon dioxide and methane mixture were measured in this study in order to identify the hydrate-forming stable region. The quadruple points at which the four phases of hydrate, water-rich liquid, carbon dioxide-rich liquid and vapor ($H-L_w-L_{CO2}-V$) coexist were determined to find the upper limit of three phase boundaries. In addition, two phase equilibria of hydrate and vapor were carefully measured and the concentration of carbon dioxide in hydrate phase was also analyzed.

Experimental Section

Materials. The methane was supplied by the Scientific Gas Products Co. and had a purity of 99.99 mol %. World Gas Co supplied the carbon dioxide with a minimum

purity of 99.9 mol %. The water was supplied from Sigma-Aldrich Chemical Co. with a purity of 99.1 mol %.

Apparatus and Procedure. A schematic diagram of the experimental apparatus used in this work is shown in Figure 1. The equilibrium cell is made of 316 stainless steel and its internal volume is about 50 cm^3 and equipped by two thermally reinforced sight glasses. The cell contents were agitated by a magnetic spin bar that was coupled with an immersion magnet placed under the cell in the bath. The bath contained about 30 L of a liquid mixture of ethanol and water, which was controlled by an externally circulating refrigerator/heater. The actual operating temperature in the cell was maintained with the PID temperature controller (JeioTech, MC-31) with ±0.1 K accuracy and was measured by a K-type thermocouple probe with a digital thermometer (Cole-Parmer, 8535-26) of which the resolution is ±0.1 K. (Every Ready Thermometer Co. Inc) The Heise Bourdon tube pressure gauge (CMM 104957, 0-200 bar range) having the maximum error of ±0.1 bar in the full-scale range was used to measure the cell pressure in the system. For the measurement of vapor compositions at a given equilibrium condition, a sampling valve (Rheodyne, 7413) having a sampling loop of about 24.36 μL was installed and connected to a gas chromatograph (Hewlett-packard, 5890A) on-line through the high-pressure metering pump (Milton Roy, 2396-31). The gas chromatograph used a thermal conductivity (TCD) and a PORAPAK-Q packed column. A vapor-sampling valve was used to perform the calibration for methane and carbon dioxide. The calibration curves for methane and carbon dioxide were fitted to the first-order and second-order polynomials, respectively. For the measurements of hydrate compositions, the specially-designed sampling port was used to obtain and analyze the hydrate samples at equilibrium conditions. It consists of two valves and small cylindrical cell. Using two

valves, the hydrate sample was transported into the cylindrical cell and allowed to decompose for analysis. The vapor resulting from dissociation of hydrate samples were analyzed using gas chromatograph. Carbon dioxide and methane gas mixture was made using two syringe pumps (ISCO Co. D Series). Since syringe pump has a function of constant flow operation, the gas mixture with known composition was introduced into the equilibrium cell and the constant pressure mode was also used to maintain the isobaric condition. The charged gas mixture was analyzed using gas chromatograph and confirmed the desired composition.

An amount of approximately 25 ml of liquid water was initially charged into the equilibrium cell using metering pump. Then, the mixed gas of carbon dioxide and methane was supplied to the equilibrium cell. After the cell was pressurized to a desired pressure with a gas mixture, the system was cooled to about 5 K below the anticipated hydrate-forming temperature. Hydrate nucleation and growth was then induced and the system pressure was decreased continuously. The consumed gas mixture was recharged using the high-pressure pump and syringe pump to maintain constant pressure. After the system pressure reached a steady state, the cell temperature was then very slowly elevated to dissociate the formed hydrates. The cell external heater was used to increase the system temperature at a rate of 1 to 2 K per hr. As the system approach the equilibrium temperature, the dissociation of hydrate phase caused the increase of system pressure. To maintain constant pressure in the system the decomposed gas was vented through the valve connected to the cell. When the amount of minute crystals remained and system pressure was kept constant at least for 8 to 10 hr after the system temperature was stabilized, the resulting temperature and pressure were considered as three phase equilibrium conditions. When the system pressure and temperature was in

equilibrium, the vapor phase was analyzed several times through gas chromatograph. The reported equilibrium composition of the vapor phase was taken as the average value. In particular, the nucleation and dissociation steps were repeated to measure the composition of hydrate phase. When the system pressure was kept constant at 0.5 K below the three phase equilibrium temperature, the hydrate sample was introduced into sampling port and analyzed using a gas chromatograph.

Results and Discussion

Three-phase equilibria ($H-L_w-V$) for the binary guest components of carbon dioxide and methane were determined at several isobaric conditions together with the quadruple points. Measured equilibrium data are tabulated in Table 1 and Table 2 and also shown in Figure 2. Measured equilibrium vapor compositions were very similar to the initial loading compositions. The $H-L_w-V$ curves of mixed hydrates were placed between simple carbon dioxide and methane hydrates. It must be however noted that above 60 mol % CO_2 concentration the $H-L_w-V$ curves of the mixed hydrates closely approached to that of the simple carbon dioxide hydrate. This phenomenon can be explained by comparing the size of both guest molecules. Methane molecules enter both small and large cavities of structure I due to their small size, while carbon dioxide molecules only occupy the large cavities. When structure I is formed with the mixed gas of carbon dioxide and methane, two species compete with each other for better occupancy. Consequently, carbon dioxide molecules are encaged in most of large cavities, while methane molecules are encaged in small cavities and a little portion of large cavities. Adisasmito and Sloan explained a similar phenomenon[8]. At high carbon dioxide concentration the upper quadruple point locus intersects with the $H-L_w-V$ curve. At an upper quadruple point one additional CO_2-rich liquid phase (L_{CO2}) coexists with hydrate,

water-rich liquid and vapor phases. According to this study, the upper quadruple point appeared above 82.50 mol % of CO_2 concentration. At temperatures higher than the upper quadruple point temperature the hydrate phase cannot exist because the quadruple locus becomes the upper limit condition of hydrate formation. The H-L_w-V equilibrium pressures were predicted from a thermodynamic model using the van der Waals and Platteeuw model[9], which related the chemical potential of water in the hydrate phase to that in hypothetical empty hydrate lattice. The overall structure of thermodynamic model for describing H-L_w-V equilibria was given in detail in our previous work[10]. All the reference properties of carbon dioxide and methane hydrate needed for model calculation were obtained from the literature[11]. The optimized Kihara potential parameters were used to describe the interaction between the guest-water molecules in the hydrate cavities and the cavity potential function. These values were optimized from the H-L_w-V equilibrium data and presented in Table 3. The predicted H-L_w-V results are in good agreement with the corresponding experimental data as shown in Figure 2. Two phase equilibrium of hydrate and vapor (H-V) measured at three different pressures were given in Table 4 and depicted in Figure 3. When the H-V equilibrium pressure is lower than 25 bar that is the lower quadruple pressure of pure methane, the H-V equilibrium lines end at the lower quadruple locus. At this lower quadruple locus, the ice phase is newly formed. Therefore, this quadruple locus becomes the lower limit condition of hydrate formation. As expected, carbon dioxide is more contained in the hydrate phase than methane over the entire range of composition. The concentration of carbon dioxide in hydrate phase increases with increasing that in vapor phase. When 40 mol % CO_2 exists in the vapor phase, the corresponding carbon dioxide compositions in the hydrate phase were found to be   93.63, 92.72 and 88.99 mol % at 20, 26 and 35 bar,

respectively. This result indicates that at lower pressure condition carbon dioxide was more preferably occupied than methane in the empty cavities of hydrates. It is expected that carbon dioxide can create a long-lived hydrate lake on the ocean floor by injection to the natural gas hydrate deposits. Injected carbon dioxide stream results in the dissociation of natural gas hydrate and subsequent growth of carbon dioxide hydrate will occur. Therefore, the formed hydrate phase is occupied mainly by carbon dioxide and the dissociated methane gas can be recovered as a useful energy source. Using the isobaric T-x diagram given in this study, carbon dioxide sequestration strategy to ocean floor can be organized.

Conclusions

The isobaric three phase (H-L_w-V) equilibria were measured for the mixtures containing two guest components of carbon dioxide and methane. Depending on the compositions of vapor phase, the equilibrium hydrate dissociation pressures were varied between two H-L_w-V curves of pure carbon dioxide and methane. The quadruple points where the four phases (H-L_w-L_{CO2}-V) coexist were also determined to examine hydrate stability limit. The hydrate phase equilibria were well predicted by the van der Waals and Platteeuw model. In addition, two phase equilibria (H-V) were determined at isobaric conditions. When the equilibrium pressure was lowered, carbon dioxide molecules were more preferably occupied than methane molecules in the empty cavities of hydrates over the entire vapor composition range.

Nomenclature

a parameter in the equations of state or radius of the spherical core

P pressure [bar]

T temperature [K]

y vapor phase composition of carbon dioxide

σ distance between the cores at zero potential energy

ε depth of the intermolecular potential well

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Table 1. Isobaric Three Phase (H-L$_w$-V) Equilibrium Data of the Carbon dioxide, Methane and Water Mixtures.

P/bar	T/K	Loading composition (mole % CO_2)	Vapor phase composition (mole % CO_2)
15	273.56	60.0	61.69
	274.76	100.0	100.00
20	273.56	20.0	26.34
	275.86	60.0	56.48
	277.16	100.0	100
26	273.16	0.0	0.00
	275.36	20.0	18.54
	277.96	60.0	61.95
	279.16	100.0	100.00
35	276.16	0.0	0.00
	278.06	20.0	20.09
	280.16	60.0	60.87
	281.46	100.0	100.00
50	279.60	0.0	0.00
	281.46	20.0	19.71
	283.26	100.0	59.89

Table 2. Upper Quadruple Points (H-L$_w$-L$_{CO2}$-V) of the Carbon dioxide, Methane and Water Mixtures.

P/bar	T/K	Vapor phase composition (mole % CO_2)
67.20	285.56	82.50
55.60	284.56	89.93
49.30	283.86	94.83
45.30	283.32	100.00

Table 3. Optimized Kihara Parameters of Carbon Dioxide and Methane.

Parameter	CH_4	CO_2
ε/k, K	153.200	168.3
σ (Å)	3.2408	2.9925
a (Å)	0.300	0.720

Table 4. Two Phase (H-V) Equilibrium Data of the Carbon dioxide, Methane and Water Mixtures at 20, 26 and 35 bar.

P/bar	T/K	Vapor phase composition (mole % CO_2)	Hydrate phase composition (mole % CO_2)
20	273.06	28.44	91.51
	274.06	40.25	93.63
	275.36	60.76	98.15
	276.26	79.44	99.65
26	273.76	12.93	66.18
	274.86	23.44	84.68
	276.26	41.46	92.72
	277.46	64.11	98.08
	278.06	83.39	99.35
35	276.56	13 .25	64.72
	277.56	25.23	73.34
	278.96	41.91	88.99
	279.86	61.13	95.23
	280.46	83.44	99.30

Figure Captions

Figure 1. Schematic diagram of the experimental apparatus used in this work: 1. Equilibrium cell ; 2. Water bath ;3. Pressure gauge ;4.Thermocouple ;5. Magnetic stirrer ;6. CO_2 sylinder ; 7. CH_4 cylinder ;8 , 9. Syringe pump ;10. Multi controller; 11. Check valve; 12. Rupture disc ;13. Line filter ;14. High pressure pump ;15. Sampling valve ;16. Helium gas ;17. Gas Chromatograph ;18. External heat exchanger ;19. High pressure pump ;20. Sampling port

Figure 2. Isobaric three phase (H-L_w-V) equilibria of the carbon dioxide, methane and water mixtures : ○, Adisasmito et al[4](CH_4 hydrate); □, Adisasmito et al[4](CO_2 hydrate); ●, This work (CH_4 hydrate); ■, This work (CO_2 hydrate); ▲, This waork (y = 20 mol% CO_2); ▼, This work (y = 60 mol% CO_2); ♦, This work (measured upper quadruple points); ▬, calculated results.

Figure 3. Two phase (H-V) equilibria of the carbon dioxide, methane and water mixtures at 20, 26 and 35 bar: Δ, vapor phase at 35 bar; ▲, hydrate phase at 35 bar; ○, vapor phase at 26 bar; ●, hydrate phase at 26 bar; □, vapor phase at 20 bar; ■, hydrate phase at 20 bar.
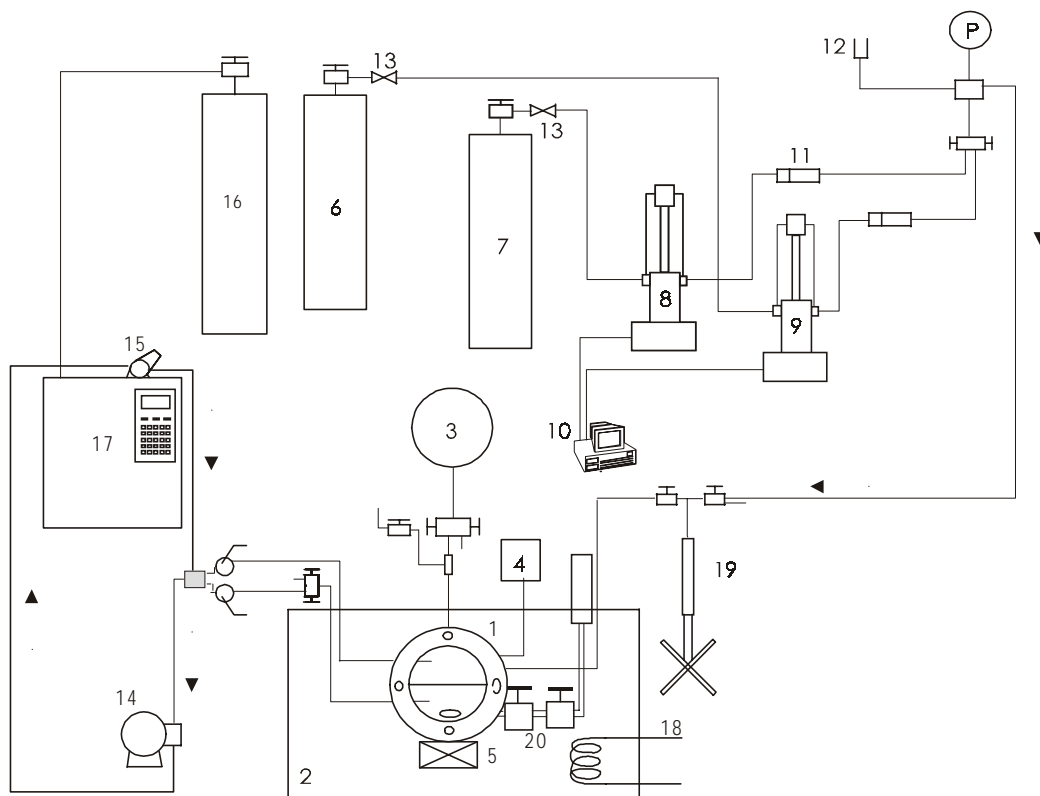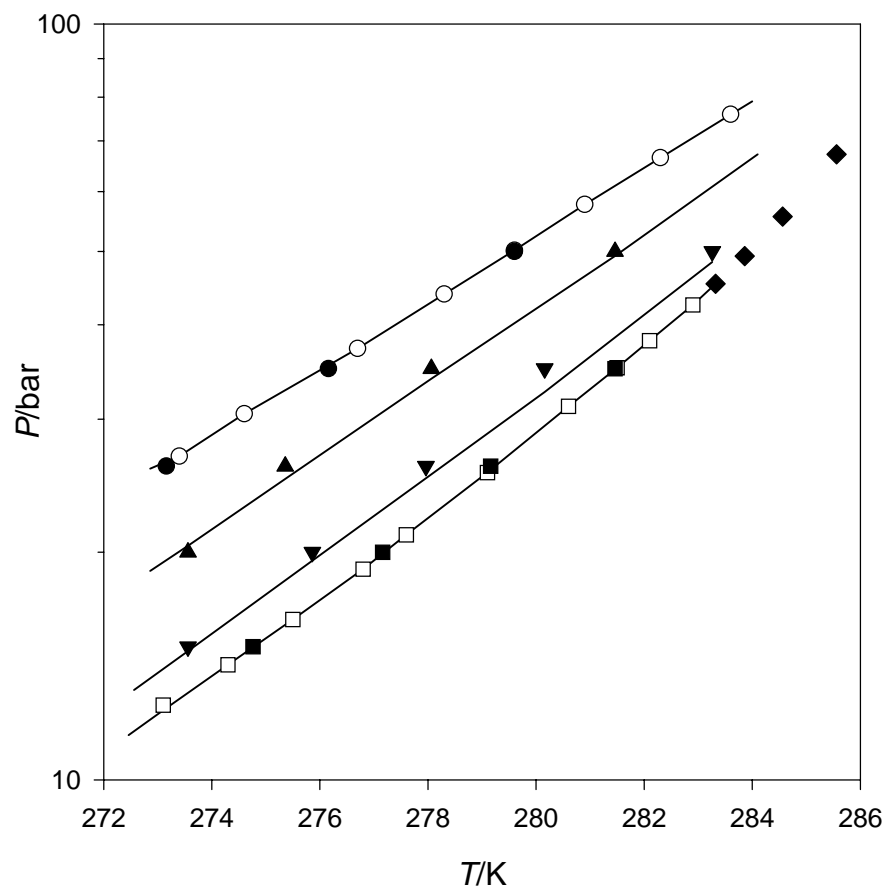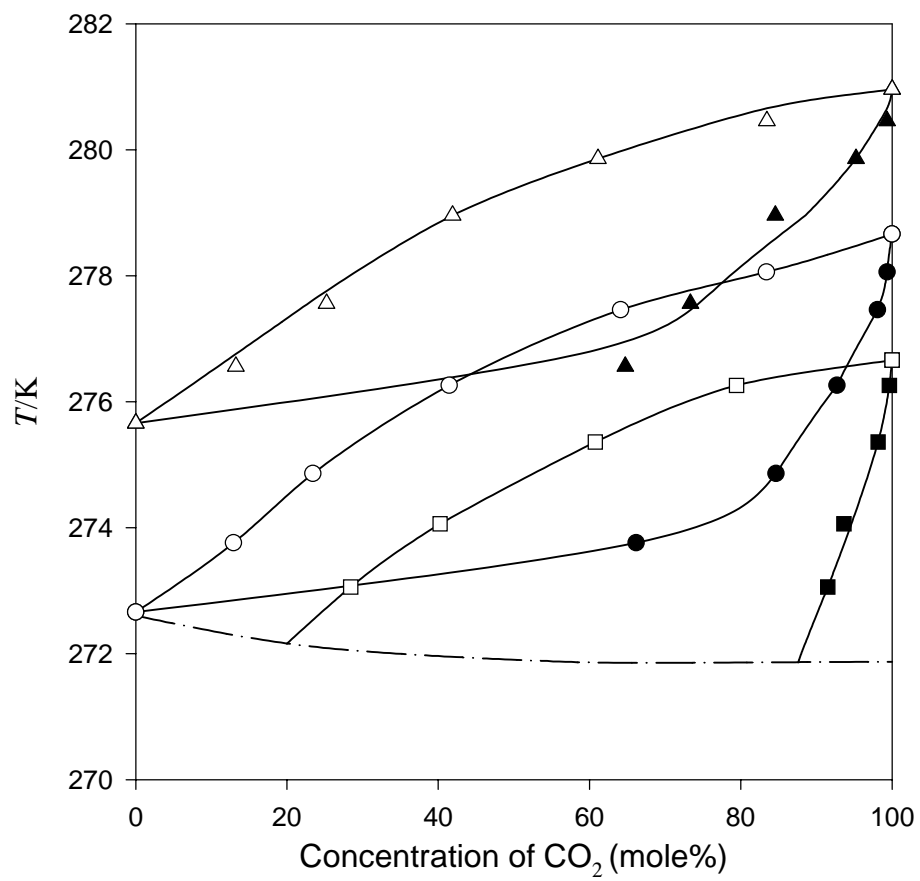
Figure 1.

Figure 2.

Figure 3.